

# Precision, Tunable Deuterated Polyethylene via Polyhomologation

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## **ABSTRACT**

The ability to introduce isotopic labeling in a controlled fashion into polymers has long been an area of keen interest, as it allows for analysis by methods such as small-angle neutron scattering. In this work, polyhomologation (also known as “C1 polymerization”) of a deuterated ylide was performed, yielding linear polyethylene of high deuterium content. Copolymerization with the protonated analog allowed for the preparation of statistical copolymers, in which linear polyethylene with a uniform and tunable amount of deuterium is obtained. The amount of deuterium present, as well as its uniform distribution, is supported by vibrational spectroscopy, size-exclusion chromatography with infrared detection, and <sup>2</sup>H nuclear magnetic resonance

spectroscopy. This technique was extended to prepare a precision triblock copolymer in which the chain-ends are selectively deuterated. All polymers reported are of narrow dispersity, and will find use in myriad measurements sensitive to deuterium labeling, most notably small-angle neutron scattering.

## INTRODUCTION

The demand for polyolefins has continued to expand worldwide, with nearly 300 million tons of plastics produced annually.<sup>1</sup> Accordingly, fundamental research into the synthesis of these macromolecules has continued unabated, with particular attention in recent years being given to the introduction of polar functional groups,<sup>2-7</sup> control over branching (length, frequency, and stereochemistry),<sup>8-13</sup> achieving ultrahigh molar mass while maintaining narrow dispersity ( $D$ ),<sup>14</sup> exploration of metal-organic frameworks as catalysts,<sup>15,16</sup> and compatibilizers for recycling of immiscible polyethylene (PE) and isotactic polypropylene (*i*PP), which constitute nearly half of all polyolefins produced annually.<sup>17</sup>

While these types of controls over polyolefin composition and structure have been areas of interest in recent years, the controllable introduction of isotopic labeling, specifically deuterium, has received far less attention. Deuterium is a broadly important label in polymer science as it allows for the use of small-angle neutron scattering (SANS) to probe features such as the relationship between number average relative molar mass ( $M_n$ ) and radius of gyration ( $R_g$ ),<sup>18</sup> self-assembly<sup>19</sup> and micellization<sup>20,21</sup> in block copolymers, and interactions of polymer blends.<sup>22-</sup><sup>25</sup> In regard to semicrystalline polymers such as PE, SANS has found significant use in structure investigations such as the function and abundance of “tie-chains,” macromolecules which traverse the amorphous region tethering crystalline domains together,<sup>26</sup> or the location of chain

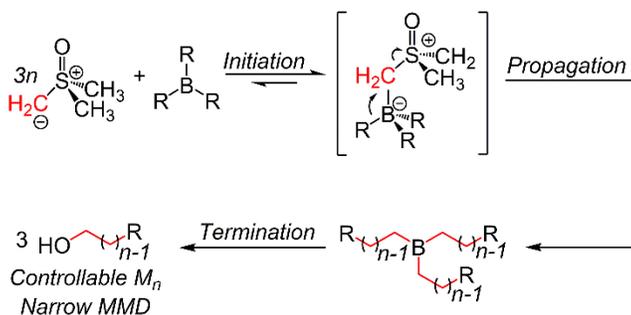
ends within this lamellar structure, which has been debated over the years.<sup>27</sup> Recent nuclear magnetic resonance (NMR) investigations suggest that chain ends exist at the interface between crystalline and amorphous regions.<sup>28,29</sup> Homogeneous and/or selective deuteration will permit fundamental measurements of isotope distribution effects on physical properties of polyolefins. For instance, differences in melting temperature, glass transition temperature, and other physical characteristics have been observed between deuterated and protonated polyolefins.<sup>30</sup> Knowledge of the magnitude of these effects will improve SANS measurements, both in experimental design and analytical models to account for deuteration effects in bulk material measurements.

With these examples in mind, the need to develop methods which allow for the precision synthesis of deuterated polyethylene (dPE) is apparent, ideally ones which allow for i) easily tunable degrees of deuteration, ii) uniform deuteration across polymer chain *or* localization of deuteration, iii) defect-free structures (*i.e.* no possibility of deformations, heterogeneity, or structural irregularities), iv) controllable molar masses, and v) narrow  $D$ . While it is certainly true that precision PE meeting these criteria is not representative of commercial PE, such polymers are very useful in measurements where small architectural impurities, such as chain-ends, are to be located. As such, the materials we describe herein are not intended to mimic commercially available PE, or to be used as a deuterated model for such macromolecules, but rather may find use in specific measurements such as chain-end location or tie-chain estimation, as well as in providing fundamental data against which to validate new theory and models. Deuterated polymers have traditionally been prepared by the polymerization of fully deuterated monomers<sup>31</sup> or saturation of unsaturated precursors using  $D_2$  in lieu of  $H_2$ . With regard to PE, both of these systems suffer drawbacks. For instance, ethylene- $d_4$  is very expensive, and standard polymerization techniques may allow for unintended short-chain branching.<sup>32</sup> Even in

very minor amounts, these branches represent architectural impurities in the resulting polymer which are undesirable for high precision measurements, even though branching typically does exist in commercial PE. Korshak and coworkers demonstrated the copolymerization of ethylene and ethylene- $d_4$  using a Ziegler catalyst system ( $(C_5H_5)_2TiCl_2 + Al(CH_3)_2Cl$ ) and, based on mass spectrometry measurements of monomer consumption, reported the resulting polymer to have a homogenous distribution of deuterium.<sup>30</sup> No spectroscopic or chromatographic analysis of the material, however, was provided to bolster this claim. With regard to the latter method,<sup>24</sup> the extent of deuteration is limited by the number of double bonds present in the precursor which are susceptible to saturation with  $D_2$  (reaching a maximum amount of deuteration of 50 % for polyacetylene), and localization of deuteration is synthetically challenging. Postpolymerization H-D exchange has reemerged as an attractive method for the preparation of dPE in recent years. In this technique, a polymer is reacted with a catalyst in the presence of a deuterium source. Crist and Nicholson first reported this approach, however expensive cyclohexane- $d_{12}$  was used as the deuterium source.<sup>33</sup> More recently, Bates and Habersberger have altered this technique to employ  $D_2$  gas.<sup>34</sup> While this method is quite useful for the preparation of identical protonated and deuterated polymers in terms of  $M_n$  and  $\bar{D}$ , the maximum amount of deuteration reported was 68%, and deuteration was not uniform across the entire molar mass distribution (MMD).

In order to address all of the goals stated above, we turned our attention to polyhomologation.<sup>35,36</sup> In this technique, an ylide, typically dimethylsulfoxonium methyllide

### Scheme 1



$[(\text{CH}_3)_2\text{S}(\text{O})\text{CH}_2]$  (**4**), transfers a methylene unit to a borane initiator, which then grows the polymer chain by one methylene unit at a time (Scheme 1). PE can be made *via* this route over a wide range of molar masses (up to  $M_n = 350 \text{ kg/mol}$ ) with narrow  $D$ .<sup>37</sup> Furthermore, the end groups can be altered, allowing for valuable post-polymerization modifications.<sup>38–40</sup> We envisioned the synthesis of a deuterated ylide for use in polyhomologation as a method for the synthesis of precision, tunable, defect-free dPE. Shea and coworkers referred to the synthesis of one such material of low  $M_n (< 1000 \text{ g/mol})$ , however no analysis of the MMD nor deuterium content was provided.<sup>41</sup> Herein, we report the results of our studies which demonstrate tunable deuteration that is uniform across both the narrow MMD and individual polymer chains, as well as the facile selective deuterium labeling of chain ends. Furthermore, we report the first full infrared (IR) and Raman spectra of these materials, which are of critical importance in understanding the molecular sequence and interpreting size-exclusion chromatography data with IR detection (SEC-IR). These precision materials will find use in probing chain conformations using SANS or other techniques sensitive to deuterium labeling, such as vibrational spectroscopy.

## EXPERIMENTAL SECTION

**Disclaimer.** Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

**General.** All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard glovebox or Schlenk-line techniques. Dimethyl sulfoxide- $d_6$

[(CD<sub>3</sub>)<sub>2</sub>SO] (D, 99.9 %), methyl iodide-*d*<sub>3</sub> (CD<sub>3</sub>I) (D, 99.5 %, stabilized with copper wire), and polyethylene-*d*<sub>4</sub> (D, 99 %) were purchased from Cambridge Isotope Laboratories, LLC, and used without further purification. Borane dimethyl sulfide complex [BH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub>] (BDMS), trimethylamine *N*-oxide dihydrate [(CH<sub>3</sub>)<sub>3</sub>NO·(H<sub>2</sub>O)<sub>2</sub>] (98 %) (TAO), benzyltributylammonium chloride [BzN(<sup>n</sup>Bu)<sub>3</sub>Cl] (99 %), CDCl<sub>3</sub> (D, 99.8 %), tetrachloroethane-*d*<sub>2</sub> (C<sub>2</sub>Cl<sub>4</sub>D<sub>2</sub>) (TCE-*d*<sub>2</sub>), (D, >99.5 %), and pentaerythritol tetrakis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) (98 %) (Irganox 1010) were purchased from Sigma Aldrich and used without further purification. Celite® 545 was purchased from Sigma Aldrich and oven dried (>160 °C) for several days before use in the glovebox. Sodium hydride (60 % dispersion in mineral liquid) was purchased from TCI America and washed thoroughly with dry hexane before use, or purchased dry (95 %) from Sigma Aldrich and used without purification. Toluene was distilled from calcium hydride (CaH<sub>2</sub>) under argon and stored under dry argon prior to use. Hexane and tetrahydrofuran (THF) were distilled from sodium under argon and stored under dry argon prior to use. 1,2,4-Trichlorobenzene (HPLC grade) was purchased from VWR for use in SEC. Monomer **4** was prepared according to literature procedures.<sup>37</sup> All other commercially available solvents and reagents were used without further purification.

**Vibrational Spectroscopy.** dPE samples prepared *via* polyhomologation were melted in a vacuum oven at 150 °C and recrystallized prior to measurements. Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR instrument with a ZnSe ATR (attenuated total reflection) single bounce crystal at 60°, using a resolution of 2 cm<sup>-1</sup> and 128 scans per spectrum using a DTGS (deuterated triglycine sulfate) detector. Samples on the ATR crystal were put in immediate contact by compression with a freshly cleaned gold-coated silicon wafer, which is IR reflective. Raman spectroscopy was performed using a DXR Raman microscope,

manufactured by Thermo Fisher, with a laser wavelength of 780 nm and laser power of 24 mW. Samples were measured on glass substrates, and the spectrum for the polymer was obtained by subtracting the spectrum of the clean glass substrate from the sample on the glass. 120 exposures at 30 s per exposure were taken. The resolution of spectra obtained is  $\pm 1 \text{ cm}^{-1}$ .

### **Nuclear Magnetic Resonance Spectroscopy.**

*Sample Preparation.* The samples were prepared by adding approximately 0.7 g of solvent stock containing 0.0059 g TCE- $d_2$  per g solvent as an internal  $^2\text{H}$  reference for quantitation, to (0.008 to 0.015) g sample in a 5 mm NMR tube. The solvent stock was 10 % (m/m) *p*-dichlorobenzene- $d_4$ , 90 % (m/m) *o*-dichlorobenzene. All masses were recorded to 0.0001 g. The samples were dissolved and homogenized by heating the tube and its contents to 130 °C using a heating block, and mixing periodically using a vortex mixer. Each sample was visually inspected to ensure homogeneity.

*Data Acquisition Parameters and Analysis.* The data were collected using a Bruker 600 MHz spectrometer equipped with a 5 mm Bruker Dual DUL high-temperature CryoProbe. The data were acquired using 2 dummy scans, 64 transients per data file, a 2.2 s acquisition time, 20 s relaxation delay, 300  $\mu\text{s}$   $^2\text{H}$  pulse at 3 W power level, and a sample temperature of 120 °C. The TCE-  $d_2$  internal standard peak at 6 ppm was integrated and set to a value of 1000. This established the integral value per mole of  $^2\text{H}$ . The polymer integral from about (0.6 to 3.0) ppm was used to determine the total moles of  $^2\text{H}$  in the polymer. Details explaining how this data was used to determine the %D in the polymers measured (with an uncertainty of  $\pm 1$  %) are provided below.

**Size Exclusion Chromatography (SEC).** High temperature size-exclusion chromatography was performed using a Polymer Char GPC-IR instrument with an IR4 detector, Wyatt

Technology Dawn Heleos II multi-angles light scattering detector (18 angles), and differential viscometer, as well as a Tosoh HT-Eco SEC instrument with differential refractive index detection. For the Tosoh instrument, narrow dispersity polystyrene standards were used for calibration. For the Polymer Char instrument, narrow dispersity polystyrene standards were used for column calibration, as well as NIST SRM<sup>®</sup> 1475a (linear, broad, HDPE), and NIST SRM<sup>®</sup> 1478 (to determine inter-detector delay and normalize photodiode response of the MALS detector), and 6 octene LLDPE standards (Polymer Char) to calibrate the IR response from the methyl and alkyl absorption bands. Calibration and data analysis was performed by proprietary software from each instrument vendor. Runs were performed at 135 °C using 1,2,4-trichlorobenzene as the mobile phase (300 mg/kg Irganox 1010 was added as antioxidant to the solvent). The stationary phase for both systems was a set of 3 Tosoh HTs columns (2 Tosoh TSKgel GMHhr-H (S) HT2, 13 µm mixed bed, 7.8 mm ID × 30 cm columns and 1 Tosoh TSKgel GMHHR-H (20) HT2, 20 µm, 7.8 mm ID × 30 cm column with an exclusion limit  $\approx 4 \times 10^8$  g/mol). The uncertainty in the molar masses obtained by this measurement is  $\pm 1.5$  %.

**Differential Scanning Calorimetry (DSC).** Measurements were performed in a Perkin Elmer DSC8500 equipped with a CLN2 liquid nitrogen chiller under a dry helium purge. Temperature calibration was performed with benzophenone and indium standards at 10 °C/min. Enthalpy was calibrated against indium. Samples were heated from room temperature to 140 °C at 10 °C/min, held for 2 min, cooled at 2 °C/min to -50 °C, held for two min, and heated to 140 °C at 10 °C/min. Enthalpies and melting temperatures were obtained from second heats.

## Synthesis of New Compounds and Polymers.

*Preparation of trimethylsulfoxonium iodide- $d_9$  (2).*  $(\text{CD}_3)_2\text{SO}$  (13.75 g, 0.176 mol) and  $\text{CD}_3\text{I}$  (50.00 g, 0.352 mol) were combined neat in a small round bottom flask, which was purged thoroughly with dry argon. The mixture was refluxed under argon for 5 d. A yellow precipitate formed over the course of the reaction. The mixture was cooled to room temperature, and excess  $\text{CD}_3\text{I}$  was distilled under argon. 40 mL acetone was added to the remaining solid, cooled to  $-78\text{ }^\circ\text{C}$ , and filtered. The solid was washed with additional cold acetone to furnish **2** as a white, crystalline solid (22.68 g, yield = 56 %). IR (ATR): (2236, 2113, 1239, 1026, 1012, 862)  $\text{cm}^{-1}$ .

*Preparation of trimethylsulfoxonium chloride- $d_9$  (3).* Compound **2** (22.89 g, 0.099 mol) and  $\text{BzN}(\text{}^n\text{Bu})_3\text{Cl}$  (32.86 g, 0.1063 mol) were combined in a biphasic mixture of dichloromethane (DCM, 200 mL) and  $\text{H}_2\text{O}$  (200 mL) and vigorously stirred for 18 h at room temperature, protected from light. The aqueous layer was isolated and washed with DCM (3 x 60 mL). The  $\text{H}_2\text{O}$  was evaporated, and the resulting white solid was recrystallized from methanol (MeOH) to yield **3** as a white, crystalline solid, which was ground into a fine powder and placed under vacuum overnight (8.50 g, yield = 68 %). IR (ATR): (2256, 2121, 1249, 1218, 1029, 912, 876)  $\text{cm}^{-1}$ . Note: Heating this mixture at any point, including during evaporation of  $\text{H}_2\text{O}$ , is not advisable, as significant H-D exchange is observed to occur (*i.e.*, resulting PEs have significantly more H content than expected).

*Preparation of dimethylsulfoxonium methylide- $d_8$  (1).* Compound **3** (2.02 g, 0.015 mol) and NaH (0.55 g, 0.023 mol) were combined in 25 mL THF and refluxed with vigorous stirring under dry argon for 4.5 h. After cooling to room temperature, the solvent was evaporated and the product was quickly extracted in dry toluene (60 mL) and filtered through Celite® 545 to yield a clear solution of **1**. The concentration was determined by titration of an aliquot with standardized

hydrochloric acid (HCl) solution with phenylphthalein as the indicator (0.16 mol/L, yield = 66 %). Note: The reaction may be performed analogously using toluene as the solvent, which does not require solvent removal at any point. NaH as a dispersion in mineral liquid may be used as well, with the mineral liquid being removed by washing with dry hexane prior to use.

*General polymerization procedure.* Monomer **1** in toluene solution was heated to 75 °C and stirred vigorously under dry argon, at which point BDMS was added quickly *via* syringe. (Note: Preparing a stock solution of BDMS in THF is advised to assist in delivering the proper amount of initiator). The solution was stirred for 15 min, at which point an aliquot was removed and added to H<sub>2</sub>O containing phenylphthalein indicator, indicating that all **1** had been consumed. Excess (6 equivalents) TAO was added under flow of dry argon, and the resulting solution was stirred at 75 °C for an additional 2 h. The solution was cooled to room temperature, concentrated, precipitated into MeOH, and isolated by decanting off the supernatant. The resulting polyethylene was washed well with MeOH, acetone, and hexanes, and dried under vacuum overnight. In H/D copolymerizations, the reaction was performed analogously, however toluene solutions of monomers **1** and **4** in the appropriate molar ratios were mixed well first before adding the BDMS initiator. The extent of deuteration in each polyethylene was determined by <sup>2</sup>H NMR and Raman Spectroscopy. Molar mass and dispersity were determined by SEC. Dispersities for all polymers were indicative of a living polymerization, although in some cases small high M<sub>n</sub> populations are observed in the SEC chromatograms (Figure S6 and S7).<sup>46</sup>

*ABA block copolymer.* Monomer **1** in toluene (0.0033 L, 1.25 mmol) was diluted with an additional 0.0360 L toluene and heated to 75 °C under argon. A 0.011 mol/L THF solution of BDMS (0.0006 L, 6.3 μmol) was added quickly, and the resulting solution was stirred vigorously

for 30 min. A 0.0020 L aliquot of the resulting solution was removed and quenched by adding to an argon purged flask containing excess TAO, which was stirred for 2 h at 75 °C. To the remaining solution, containing 3.2 μmol active initiator, was added *via* cannula monomer **4** (0.0295 L, 13.30 mmol), preheated to 75 °C. This solution was stirred vigorously for 30 m, at which point another aliquot (0.0030 L) was removed and quenched in a similar fashion. To the remaining solution, containing 3.0 μmol active initiator, was added monomer **1** (0.0017 L, 0.64 mmol). This solution was stirred vigorously for 30 m, at which point TAO (0.0125 g, 0.11 mmol) was added. The resulting solution was stirred for 2 h at 75 °C. The solution was concentrated under vacuum, and the resulting polymer was precipitated into MeOH. The supernatant was decanted, and the resulting polyethylene was washed well with MeOH, acetone, and hexanes, and dried under vacuum (0.1502 g). <sup>2</sup>H NMR determined the extent of deuteration to be 8.4 %. Raman spectroscopy determined the extent of deuteration to be 9%. Aliquots were isolated by removing all solvent *in vacuo*, followed by rigorous washing of the resulting solids with MeOH, acetone, and hexanes, before injection into the SEC. Aliquot 1:

$M_n$  (theor.) = 942 g/mol,  $M_n$  (actual) = 491 g/mol,  $D = 1.12$ .

Aliquot 2:  $M_n$  (theor.) = 20628 g/mol,  $M_n$  (actual) = 23761 g/mol,  $D = 1.13$ .

Aliquot 3:  $M_n$  (theor.) = 21580 g/mol,  $M_n$  (actual) = 25061 g/mol,  $D = 1.13$ . Note: Blocks 2 and 3 are both of higher DP than predicted, indicating that too much initiator may have been removed during removal of the first aliquot, thereby decreasing the concentration of active initiator. The measured  $M_n$  of block 1 appears lower than expected due to difficulty calibrating the SEC at low molar mass.

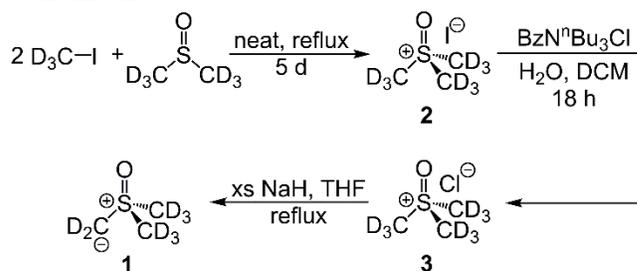
## RESULTS AND DISCUSSION

**Monomer Synthesis.** Our target monomer, dimethylsulfoxonium methylide- $d_8$  [(CD<sub>3</sub>)<sub>2</sub>S(O)CD<sub>2</sub>] (**1**), was prepared analogously to its protonated analog, as summarized in Scheme 2.<sup>37,42</sup>

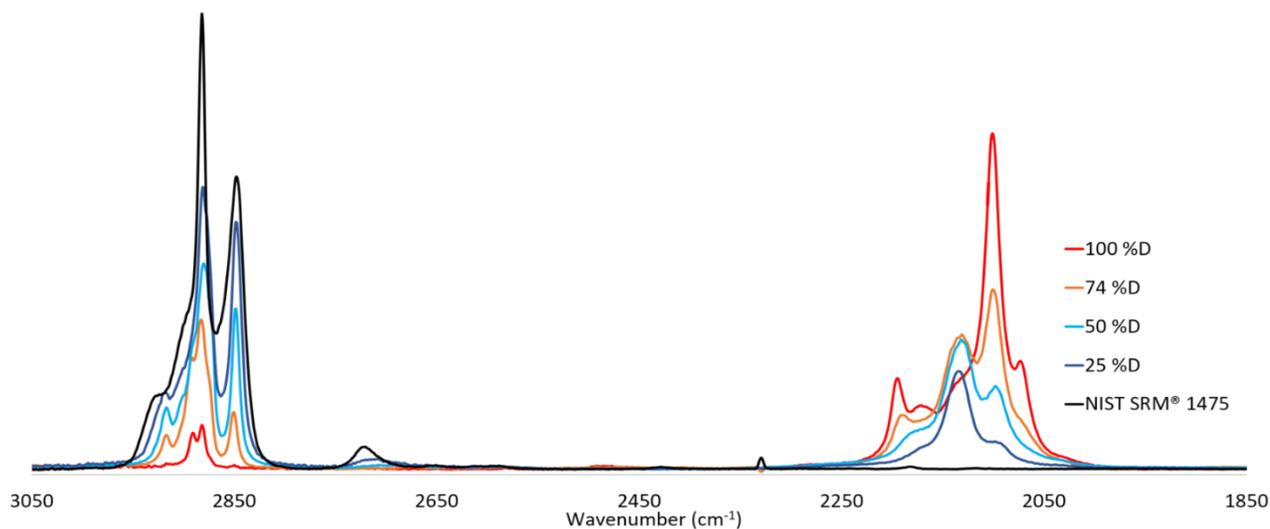
Although the reagents used in this synthesis are of high isotopic purity, the possibility remained that H-D exchange with solvents, especially H<sub>2</sub>O, could have occurred during the course of these reactions. Efforts to quantitatively assess the extent of deuteration of any of these materials was not possible due to significant H-D exchange during mass spectrometry experiments.

Accordingly, the extent of deuteration could not be determined until after polymerization.

**Scheme 2**



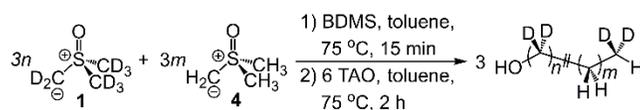
**Synthesis of dPE.** Monomer **1** was polymerized using borane dimethyl sulfide [BH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub>] (BDMS) as the initiator at 75 °C, as summarized in Scheme 3 (n:m = 100:0).<sup>37</sup> Termination with trimethylamine *N*-oxide dihydrate (TAO) yielded dPE with a hydroxyl end-group. Analysis of this material by <sup>2</sup>H NMR spectroscopy using tetrachloroethane- $d_2$  (TCE- $d_2$ ) as an internal standard revealed the deuterium content to be 98.5 %, suggesting that only minor H-D exchange had occurred during the synthesis of **1**. Details regarding the <sup>2</sup>H NMR technique and subsequent analysis are provided below. Raman spectroscopy further revealed that the resulting dPE was highly deuterated, with C-D stretches observed at 2071 cm<sup>-1</sup>, 2100 cm<sup>-1</sup>, and 2194 cm<sup>-1</sup>, and only



**Figure 1.** Partial Raman spectra of deuterated polyethylenes, and NIST SRM<sup>®</sup> 1475 for reference. The small sharp band near 2330  $\text{cm}^{-1}$  is due to atmospheric nitrogen ( $\text{N}_2$ ).

low-intensity peaks in the typical C-H stretching region (Figure 1). Specifically, the peaks at 2100  $\text{cm}^{-1}$  and 2194  $\text{cm}^{-1}$  are consistent with the symmetric and antisymmetric C-D stretching of  $\text{CD}_2$  groups, respectively,<sup>43</sup> while the peak at 2071  $\text{cm}^{-1}$  is attributed to the symmetric C-D stretch of  $\text{CD}_3$  end group.<sup>44</sup> Integration of these peaks relative to C-H stretching peaks suggested the deuterium content to be nearly identical to that determined by NMR (95 %). This approximate agreement is remarkable, since the C-D and C-H stretch regions of the polyethylene vibrational spectrum are known to contain additional bands due to combination frequencies, overtone frequencies, and Fermi resonance for both isolated single chains<sup>45</sup> and crystals.<sup>46</sup> Size-exclusion chromatography with refractive index (RI) detection calibrated against narrow dispersity PS standards revealed the  $M_n$  of the resulting polymer to be 16.7 kg/mol, slightly deviating from the theoretical  $M_n$  of 17.8 kg/mol,<sup>47</sup> with a narrow dispersity of 1.25. Together,

### Scheme 3



these data demonstrate that polyhomologation can indeed serve as a method to produce highly deuterated, precision dPE.

**Statistical Copolymers.** For a controlled polymerization, it was of interest to determine whether the ratio of H/D could easily be controlled through copolymerization, and whether the extent of deuteration would be uniform across both the MMD and individual chains in the resulting polymers. A series of dPE samples (target  $M_n \approx 18.0$  kg/mol) was prepared *via* polyhomologation with varying ratios of **1** and its protonated analog, **4** (Scheme 3).

Determination of the relative reactivity ratios of monomers **1** and **4** was not possible, unfortunately, given that the reaction occurs too quickly to follow by NMR. Accordingly, the relative reactivity ratios were assumed to be similar, with support by SEC-IR and Raman data of the resulting dPEs (*vide infra*). Again, the deuterium content was measured by  $^2\text{H}$  NMR (Table 1), which showed decreasing deuterium content as the ratio of **1** to **4** was decreased, as expected. Furthermore, for each copolymer, SEC provided  $M_n$  values close to those expected, with narrow  $D$ . The melting temperature of each copolymer was also measured by differential scanning calorimetry (DSC) after slow cooling from the melt. The melting temperature of the 25% D sample (Sample IV, Table 1) at 130.4 °C corresponds well to a previous literature report of a statistically deuterated polyethylene (30% D,  $M_w = 14$  kg/mol), measured at 130.6 °C.<sup>33</sup>

**Table 1.** Statistical copolymerizations of **1** and **4**.

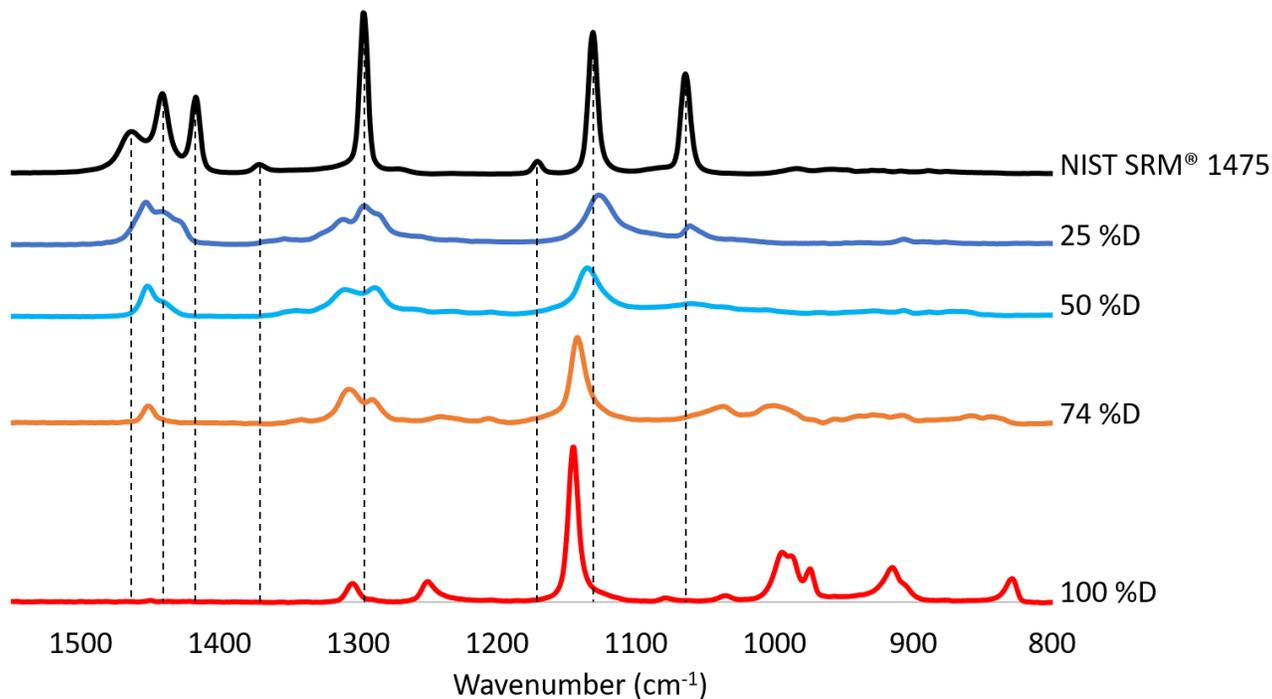
Entry	$M_n$ (theor.) (kg/mol) <sup>a</sup>	$M_n$ (kg/mol) <sup>b</sup>	$M_n$ (kg/mol) <sup>c</sup>	$\bar{D}^b$	$\bar{D}^c$	%D (theor.) <sup>d</sup>	%D (NMR) <sup>e</sup>	%D (Raman) <sup>f</sup>	$\nu(\text{C-C})$ ( $\text{cm}^{-1}$ ) <sup>g</sup>	$T_m$ ( $^{\circ}\text{C}$ ) <sup>h</sup>
I	17.8	16.7	16.1	1.25	1.25	100	98.5	95	1144	127.8
II	18.5	20.3	20.3	1.16	1.20	74	74.7	73	1142	130.7
III	19.3	17.6	17.8	1.18	1.20	50	50.3	53	1139	131.7
IV	17.6	13.4	13.4	1.32	1.36	25	25.0	28	1128	130.4

<sup>a</sup>Defined as  $[(\text{molar mass CH}_2) \times \{([\mathbf{1}] + [\mathbf{4}]) / [\text{BDMS}]\}] / 3$ , assuming 100 % conversion. Determined by SEC with 1,2,4-trichlorobenzene as the eluent at 135  $^{\circ}\text{C}$  using <sup>b</sup>RI and <sup>c</sup>IR concentration detection, calibrated against narrow dispersity PS standards and Mark Houwink parameters ( $a = 0.725$ ,  $K = 40.6 \times 10^{-5}$  dL/g). <sup>d</sup>Determined by molar ratio of monomers **1** and **4** in reaction mixture before addition of BDMS. <sup>e</sup>Determined by <sup>2</sup>H NMR at 120  $^{\circ}\text{C}$  with TCE-*d*<sub>2</sub> as an internal standard (concentration error  $\pm 1$  %). <sup>f</sup>Determined by integration of C-H and C-D stretching regions of Raman spectra. <sup>g</sup>Determined by Raman spectroscopy (peak  $\nu(\text{C-C})$  error  $\pm 1$   $\text{cm}^{-1}$ ). <sup>h</sup>Peak maximum determined by DSC on second heat after slow cooling from the melt.

**Vibrational Spectroscopy.** Raman spectroscopy of these samples displayed systematic changes in the amount of C-H vs. C-D stretching observed as a function of the theoretical deuterium content (Figure 1). Notably, C-H stretching is present in sample I (100 %D, Table 1), providing additional evidence that small amounts of unavoidable H-D exchange occurred during the synthesis of **1**. The ratios of the integrated areas under the C-H and C-D stretches were calculated for each sample as well, and closely match the %D values determined by NMR, indicating that Raman spectroscopy can be used as a convenient method for approximating deuterium content in partially deuterated PE. The symmetric C-C stretching frequency is also observed to change as a function of deuteration. In sample IV (25 %D), the C-C stretching is observed at 1128  $\text{cm}^{-1}$ , slightly below that of 100 % protonated PE, such as NIST Standard Reference Material (SRM<sup>®</sup>) 1475 [ $\nu(\text{C-C}) = 1131$   $\text{cm}^{-1}$ , Figure 2]. However, as the %D is increased, this frequency moves to higher wavenumbers, eventually being observed at 1144  $\text{cm}^{-1}$  for sample I (100 %D), nearer the value expected for fully deuterated PE (1146  $\text{cm}^{-1}$ ).<sup>48</sup> The

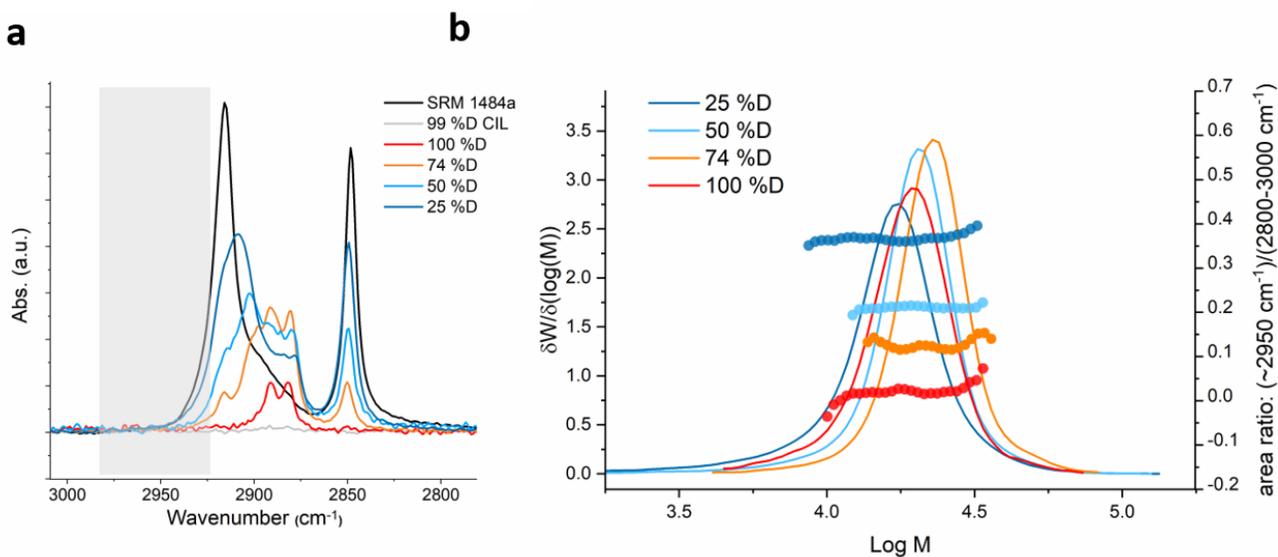
position of the symmetric C-C stretch peak depends on the degree of conformational disorder and the isotopic sequence along the chain. Increasing conformational disorder (decreasing crystallinity) is known to blueshift the symmetric C-C stretch peak by approximately  $4\text{ cm}^{-1}$ .<sup>49</sup> The isotopic sequence will have two competing effects on the C-C stretch peak position: the disruption of interchain interactions in the polyethylene crystal due to deuterium defects will blueshift the peak approximately  $2\text{ cm}^{-1}$ ,<sup>50</sup> whereas the completely perdeuterated chain exhibits a redshift in peak position relative to the protonated chain. The position of the C-C stretch peak is therefore non-monotonic with increasing deuteration; at low degrees of deuteration the peak exhibits a blueshift due to the loss of interchain interactions and possibly conformational order. Both effects also explain the loss of the  $1418\text{ cm}^{-1}$  peak in the sample IV (25 %D) spectrum. The increasing redshift with increasing deuteration for samples I through III suggests a C-C stretching mode that includes both  $\text{CH}_2$  and  $\text{CD}_2$  segments that approaches the perdeuterated peak position as the degree of deuteration increases. The  $\text{CD}_2$  bending frequencies for sample I (100 %D) are both well resolved, and can be observed at  $994\text{ cm}^{-1}$  and  $974\text{ cm}^{-1}$ , nearly identical to those reported for fully deuterated PE.<sup>51</sup> As the amount of deuterium decreases, these signals decrease in intensity, while the  $\text{CH}_2$  bending increases steadily (Figure 2). Taken together, these spectroscopic data demonstrate the increasing amount of deuterium in the PE samples as a function of the increasing feed ratio of deuterated monomer, and that Raman spectroscopy can serve as an accessible tool to evaluate the amount of deuterium present in PE.

Additionally, the Raman spectra can also be used to determine C-C sequences that are *not* present in significant quantities in samples II through IV. Either block copolymer or gradient copolymer sequences would have large runs of consecutive  $\text{CD}_2$  and  $\text{CH}_2$  units present along the



**Figure 2.** Partial Raman spectra of partially deuterated polyethylenes, and NIST SRM<sup>®</sup> 1475 for reference. Prior work on the vibrational spectra of copolymer systems has indicated that peak positions of CH<sub>2</sub> vibrational modes overlap the frequencies observed in PE when as few as 5 consecutive CH<sub>2</sub> units are present on the chain.<sup>52</sup> Therefore, block or gradient copolymer-like sequences should have peaks attributed to both protonated and perdeuterated PEs, which are not observed in samples II through IV for the C-C symmetric stretch peak, indicating that these species are in fact statistical copolymers and that deuteration is uniform across the polymer chains.

**Size-Exclusion Chromatography.** Given the distinct vibrational spectra for each dPE sample, we decided next to perform SEC-IR to determine the change in detector ratios as a function of deuteration. Typically, this technique has been used to determine short-chain branching (SCB) content in linear low-density polyethylene (LLDPE) by determining the ratio of the absorbances at the methyl asymmetric C-H stretching frequency (centered at approximately 2950 cm<sup>-1</sup>) and



**Figure 3.** a) Partial IR spectra of dPE samples. Grey box centered at  $\sim 2950 \text{ cm}^{-1}$  represents approximate location of secondary IR filter on SEC. Absorbance area of C-H and C-D stretching is normalized for comparison ( $2000\text{-}3000 \text{ cm}^{-1}$ , see Figure S5 for full spectra b) SEC-IR of dPE samples.

the entire alkyl C-H stretching region ( $2800 - 3000 \text{ cm}^{-1}$ ) and comparing against a calibration curve.<sup>53</sup> With regard to our series of dPEs, no methyl groups are expected, however each displays distinct IR spectra, with the intensity of each peak in the C-H stretching region (the asymmetric C-H stretch at  $2920 \text{ cm}^{-1}$  and the symmetric C-H stretch at  $2850 \text{ cm}^{-1}$ ) decreasing as deuterium content increases (Figure 3a). This leads to distinct differences in voltage response of the two IR concentration detectors for samples I-IV (Figure S7 and Figure 3b) measured across the entire chromatogram. As expected from observing the C-H stretching region of the IR spectra (Figure 3a), the ratio of the signal at  $2950 \text{ cm}^{-1}$  to the entire C-H stretching region decreases systematically, and remains constant over the entire MMD. Unfortunately, while this information indicates uniform deuteration across the MMD, it is not sufficient to infer that monomers **1** and **4** have similar reactivity ratios leading to uniform deuteration across each polymer chain.

There is potential to be able to use IR flow through detectors to measure deuterium content based on the preliminary findings here, as the average ratio of the IR detector signal is proportional to the measured deuterium content by NMR and Raman; however, further studies and cross-validation experiments would have to be conducted to determine the effects of distributions of C-H and C-D stretches on the IR signal and determine appropriate calibration methodologies, which is beyond the scope of this study. Lastly, Kang and coworkers have demonstrated the use of SEC-IR to measure deuterium content in PE.<sup>54</sup> Given the higher accuracy inherent in NMR measurements, and the need for analogous fully protonated PE for the highest accuracy in the method of Kang, these measurements were not explored fully in this study.

**<sup>2</sup>H NMR.** In a typical experiment, integration of the CD<sub>2</sub> resonance of a known mass of PE vs. integration of a known mass of the internal standard, TCE-*d*<sub>2</sub>, provided the %D. However, it should be noted that the molar mass of the repeat unit CD<sub>2</sub> is ~2 g/mol greater than that of CH<sub>2</sub>. *This difference in mass must somehow be accounted for during mol %D calculations*, as the total number of moles of H and D in a sample of a given mass will change depending on how much deuterium is present. Therefore, we have accounted for this change in mass in our calculations, and recommend this approach in determining %D, as the values obtained are of high accuracy. As a proof of concept, we analyzed a commercially available sample of dPE (99 %D) obtained from Cambridge Isotopes Laboratories by <sup>2</sup>H NMR. Before taking the approach described below (*i.e.* assuming the polymer repeat unit mass was 14 g/mol) we included only moles <sup>1</sup>H in the denominator of the equation:

$$\text{mol \% } ^2\text{H (D)} = [\text{mol } ^2\text{H (measured)} / \text{mol } ^1\text{H (from mass)}] \times 100 \%$$

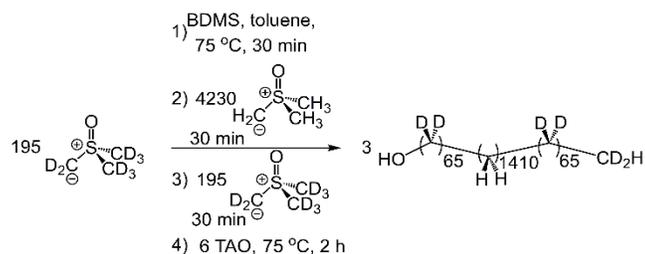
which provides 86.6 %D. However, once accounting for moles of both  $^1\text{H}$  and  $^2\text{H}$  in the denominator, using the equation:

$$\text{mol \% } ^2\text{H (D)} = \{ \text{mol } ^2\text{H (measured)} / [\text{mol } ^2\text{H} + \text{mol } ^1\text{H (from mass)}] \} \times 100\%$$

we measured 99.1 %D, nearly identical to the reported value. An example of how this calculation was performed, and the values obtained, is provided in the Supporting Information.<sup>48</sup>

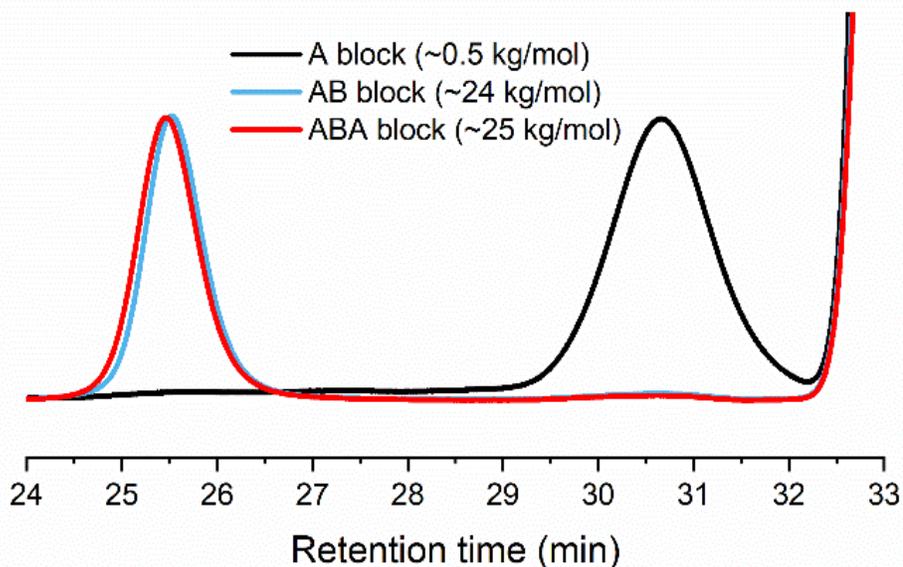
**Synthesis of Block Copolymer.** The ongoing debate over the location of chain ends in semicrystalline PE will require high precision materials in order to perform the most accurate measurements. Wutz and coworkers have recently made notable advancements in this area through the use of solid-state  $^2\text{H}$  NMR of copolymers composed of protonated and deuterated PE blocks synthesized from ethylene gas using a Co(III) catalyst.<sup>29</sup> The  $^2\text{H}$  NMR experiments demonstrated that the PE chain ends are preferably incorporated into the crystalline lamellae, in agreement with previous  $^{13}\text{C}$  NMR experiments.<sup>28</sup> With monomers **1** and **4** in hand, and given the fact that polyhomologation is a living polymerization as well, we determined it would be valuable to investigate the use of polyhomologation as an additional route to similar block copolymers. While the polymers described by Wutz are certainly suitable for the measurements described, polyhomologation may allow for more controllable and precise tuning of the resulting polymers, as the DP of each block can be controlled through modulation of monomer added, rather than reaction time. Specifically, we targeted an ABA triblock copolymer, in which the A blocks are short segments of dPE made from **1**, and the B block is a higher DP PE made from **4**.

### Scheme 4



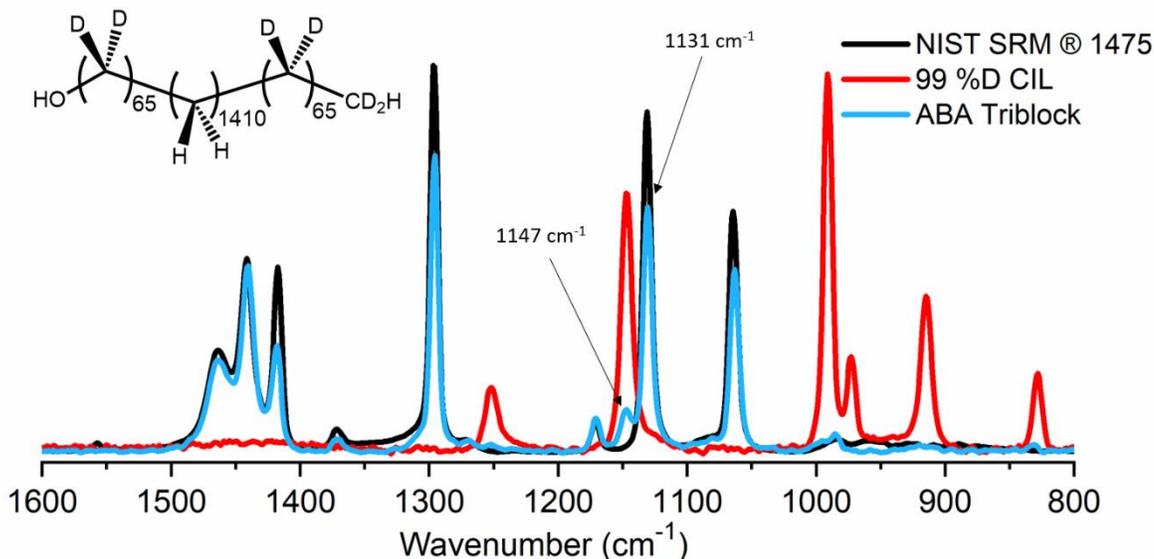
Indeed, such a PE was easily prepared as summarized in Scheme 4, with targeted A blocks of *ca.* DP = 65, and a targeted B block of *ca.* DP = 1410 (theoretical  $M_n = 21.6$  kg/mol). Analysis of aliquots removed before addition of the following monomer by SEC showed a steady increase in the molar mass of each block (Figure 4) with the molar mass of the entire triblock copolymer found to be 25.1 kg/mol ( $D = 1.13$ ) with comparable results of the final triblock copolymer obtained by SEC-IR (Figure S8).

The amount of deuterium present in the ABA triblock copolymer was expected to be 9 % based on the molar ratios of **1** and **4**.  $^2\text{H}$  NMR analysis revealed the actual amount of deuterium



**Figure 4.** SEC chromatograms for aliquots taken from synthesis of ABA triblock copolymer *via* polyhomologation.

to be 8.4 %, indicating not only that the amount of deuterium in PE can be tuned easily in polyhomologation, but that it can be localized in different regions of interest for various applications. Again, integration of the C-H and C-D stretching regions of the Raman spectrum provides an estimate of the extent of deuteration (9 %) that is consistent with the value obtained by NMR. However, unlike the random copolymers, the C-H and C-D stretches for the triblock copolymer are well defined, maintaining shapes similar to those of pure protonated and deuterated PE, respectively, indicating that the local environment around a given CD<sub>2</sub> or CH<sub>2</sub> unit is the cause of the loss of definition of the symmetric and antisymmetric stretching frequencies, rather than simply the amount of deuterium in the sample as a whole (Figure S3).<sup>48</sup> Furthermore, unlike the case of the random copolymers discussed above, two distinct C-C stretching modes are observed at 1131 cm<sup>-1</sup> and 1147 cm<sup>-1</sup> (Figure 5) indicating that the blocks are indeed fully isolated from one another and that gradients do not exist between blocks.



**Figure 5.** Raman spectrum of ABA triblock copolymer with selected peaks labeled (all values in cm<sup>-1</sup>). NIST SRM® 1475 and 99 %D dPE, obtained from Cambridge Isotopes Laboratory, are included for reference.

## CONCLUSION

Polyhomologation has been used in the past to prepare precision PE for a variety of uses. In this work, we have extended the use of this method to prepare precision dPE in which the amount of deuteration can easily be tailored, and is uniform across the narrow MMD and individual chains. These materials will prove useful for tie-chain estimation and determination of domain spacing as a function of deuterium content, the results of which will be reported in due course. Furthermore, by taking advantage of the fact that this is a living polymerization, block copolymers may be prepared. As a proof of concept, we have prepared an ABA triblock copolymer, in which the end groups are deuterated. This type of material should prove very useful in location of end-groups in semicrystalline PE with SANS and NMR.

## ASSOCIATED CONTENT

### **Supporting Information.**

The following files are available free of charge.

Supporting IR, Raman, and NMR spectra, chromatograms, and sample mol %D calculation by  $^2\text{H}$  NMR (PDF).

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

*D*, dispersity; PE, polyethylene; iPP, isotactic polypropylene; SANS, small-angle neutron scattering;  $R_g$ , radius of gyration; NMR, nuclear magnetic resonance; dPE, deuterated polyethylene; MMD, molar mass distribution; IR, infrared; SEC-IR, size-exclusion chromatography with infrared detection; BDMS, borane dimethyl sulfide; TAO, trimethylamine *N*-oxide dehydrate; TCE, tetrachloroethane; DCM, dichloromethane; MeOH, methanol; THF, tetrahydrofuran;  $M_n$ , number average molar mass; SRM, standard reference material; SCB, short-chain branching; LLDPE, linear low-density polyethylene; HDPE, high-density polyethylene; MALS, multi angles light scattering; DP, degree of polymerization; DSC, differential scanning calorimetry.

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